

Synthesis of perfluoroalkyl nitroborates: structure of Cs[(C₂F₅)₃BNO₂]

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Dedicated to Professor K.O. Christe on the occasion of his 65th birthday

Abstract

(CF₃)₂BNMe₂ reacts with CF₃(CF₂)_nI/tetrakisdimethylaminoethylene (TDAE) to form the dimethylamine boranes CF₃(CF₂)_n(CF₃)₂-B·NHMe₂ (*n* = 1 (**2**), 3 (**3**)). Reacting C₂F₅I with Br₂BNMe₂ and TDAE, (C₂F₅)₃B·NHMe₂ (**4**) was obtained in low yield. Compounds **2–4** react with ozone in CsOH solution to form the corresponding nitroborates

Cs[CF₃(CF₂)_n(CF₃)₂BNO₂] (**2a**), (**3a**) and Cs[(C₂F₅)₃BNO₂] (**4a**). The structure of **4a** has been determined by X-ray diffraction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Boron; Perfluoroalkyl group; Crystal structure

1. Introduction

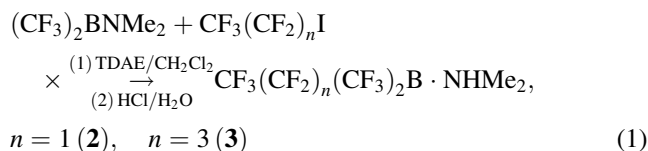
Previous studies have shown that the CF₃ groups attached to boron drastically change the properties of boranes compared to their non-fluorinated analogs [1,2]. The ammine borane (CF₃)₃B·NH₃ is one remarkable example. Though it can be formally regarded as a complex between the still unknown free borane (CF₃)₃B and ammonia, the BN bond is extraordinary strong, and dissociation into borane and NH₃ does not occur at temperatures below 260 °C, above which complete decomposition takes place. The boron atom in (CF₃)₃B·NH₃ is effectively shielded by the high fluorine content of its van der Waals surface and oxidation and halogenation reactions at nitrogen do not affect the BC bonds [3,4]. These unique properties result from the strong electron withdrawing power of the CF₃ groups and from the lack of back donation which distinguished this ligand from halogens like chlorine.

The CF₃ group may be regarded as the smallest of the perfluoroalkyl groups CF₃(CF₂)_n. Replacement of one of its fluorine atoms by another CF₃ group increases its bulkiness whereas its electronic properties are hardly affected. Little is known about boron species bearing perfluoroalkyl groups larger than CF₃ despite the fact that two tri-coordinated boron species bearing a C₃F₇ group were obtained by Chivers [5] in 1967. Recently, perfluoroalkyltrifluoroborates

[R_fBF₃][−] (R_f = C_nF_(2n+1) (*n* = 3, 6)) have been described by Frohn and Bardin [6]. The aim of the present investigation is to elucidate, how many larger perfluoroalkyl groups can be attached to boron and to compare the properties of these novel species with those of derivatives of (CF₃)₃B.

2. Results and discussion

One approach to the preparation of boranes bearing bulkier perfluoroalkyl substituents is the synthesis of CF₃(CF₂)_n(CF₃)₂B derivatives with *n* > 0. This was achieved by reacting (CF₃)₂BNMe₂ with C₂F₅I or C₄F₉I in the presence of tetrakisdimethylaminoethylene (TDAE) according to Eq. (1). TDAE acts as a reducing agent for C₂F₅I or C₄F₉I. Similarly, the TDAE/CF₃I reagent has been used to transfer CF₃ groups to boron and silicon [7].



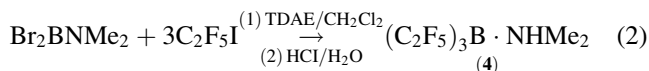
After work up, the dimethylamine boranes CF₃(CF₂)_n(CF₃)₂B·NHMe₂ *n* = 1 (**2**), *n* = 3 (**3**) were obtained in moderate yield.

In order to see how many perfluoroethyl groups could be attached to boron, we reacted C₂F₅I with Br₂BNMe₂ according to Eq. (2). Work up of the reaction mixture led to the isolation of triply substituted reaction product (**4**) as a

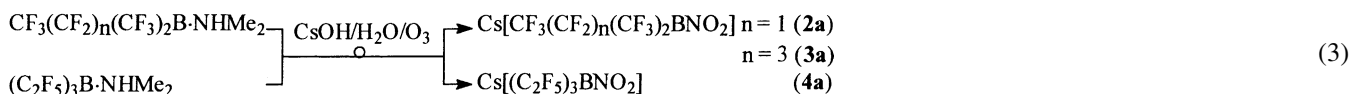
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colorless liquid in 12% yield. In addition, the doubly substituted reaction product $(C_2F_5)_2BF \cdot NHMe_2$ was detected by ^{19}F NMR spectroscopy in the crude reaction mixture.



The easiest way to remove the alkyl groups from nitrogen and to convert **2–4** into salts is the oxidation of the nitrogen atom using ozone under alkaline conditions according to Eq. (3). This method, which has been successfully employed for converting $(CF_3)_3B \cdot NHEt_2$ into $Cs[(CF_3)_3BNO_2]$ [3], furnished the nitroborates **2a–4a** in high yields. The fate of the methyl groups is unknown. The Cs-nitroborates are only slightly soluble in cold water and precipitate from the cooled reaction mixture.



2.1. Properties and spectra

All of the novel boron compounds are air-stable. In general, the physical properties of **2–4** differ from $(CF_3)_3B \cdot NHMe_2$. Despite their higher molecular weight, all are significantly more volatile and show lower melting

points. Obviously the larger number of fluorine atoms in the perfluoroalkyl groups decreases the intermolecular forces. Moreover, the melting points of the Cs-borates **2a, 3a** (65–70 °C) and **4a** (165–170 °C) are lower than for $Cs[(CF_3)_3BNO_2]$ which does not melt before decomposition. The thermal stability of **2a–4a** is the same as for $Cs[(CF_3)_3BNO_2]$, that is they all decompose explosively above 260 °C. The Cs salts **2a–4a** are only moderately soluble in water but are exceedingly soluble in organic solvents like acetone or acetonitrile.

Little is known about the NMR spectroscopic details of perfluoroalkyl groups greater than CF_3 bonded to boron. Such data are given in Table 1. The ^{19}F resonance of the B– CF_2 –C group like in $[(C_2F_5)_3BNO_2]^-$, $[C_2F_5(CF_3)_2BNO_2]^-$, and $[C_4F_9(CF_3)_2BNO_2]^-$ is located at $-120 (\pm 2)$ ppm, with

a $^2J_{(BF)}$ coupling constant of 17–18 Hz. The ^{13}C resonances of B– CF_2 –C groups are located near 123 ppm, with $^1J_{(CF)}$ coupling constants of 286 (± 2) Hz and $^2J_{(CF)}$ coupling constants of 31 (± 3) Hz.

The characteristic vibrational frequencies of the NO_2 groups in **2a–4a** are given in Table 2. They are of diagnostic

Table 1
NMR spectral data of **2–4a**

	2	2a	3	3a	4	4a
1H						
$\delta(NCH_3)$	2.84		2.98		3.04	
$\delta(NH)$	6.1		6.9		6.7	
^{19}F						
$\delta(BCF_3)$	-62.3	-65.0	-61.7	-64.5		
$^2J_{(BF)}$						
$\delta(BCF_2-)$	-122.1	-125.0	-119.2	-121.9	-117.1	-120.4
$^3J_{(FF)}$		4.4			4.8	
$\delta(C-CF_3)$	-83.6	-83.5	-82.6	-82.4	-81.8	-81.4
$\delta(CF_2-CF_2-CF_2)$			-121.5	-121.7		
$\delta(CF_2-CF_2-CF_3)$			-126.8	-126.8		
^{11}B						
$\delta(B)$	-12.1	-9.3	-11.7	-9.2	-9.1	-7.3
^{13}C						
$\delta(NCH_3)$	43.0		42.7		44.4	
$\delta(BCF_3)$	132	130.2	131.3	130.1		
$^1J_{(CF)}$	303	302	303	300		
$^1J_{(BC)}$		82	77.5	75		
$\delta(B-CF_2-)$	121	120	123.8	121.6	120.7	120
$\delta(-CF_2-CF_3)$	122.0	121.5	118.8	118.7	121.2	122
$^1J_{(CF)}$	285.2	286.0	287.2	287.6	286	286
$^2J_{(CF)}$	32.5	32.5	33.6	33.6	33	29
$\delta(CF_2-CF_2-CF_2)$			113.1	113.0		
$^1J_{(CF)}$			263.6	264		
$^2J_{(CF)}$			28.5/34.9	29/34.5		
$\delta(CF_2-CF_2-CF_3)$			110.6	110.5		
$^1J_{(CF)}$			269.3	268.6		
$^2J_{(CF)}$			37.5	38.4		

Table 2
The characteristic frequencies of the NO₂ group (cm⁻¹)

	$\nu_{\text{as}}\text{NO}_2$	$\nu_{\text{s}}\text{NO}_2$	$\delta_{\text{s}}\text{NO}_2$
Cs[(CF ₃) ₃ BNO ₂] ^a	1481	1398	796
2a	1480	1394	783
3a	1478	1391	763
4a	1471	1383	777

^a [3].

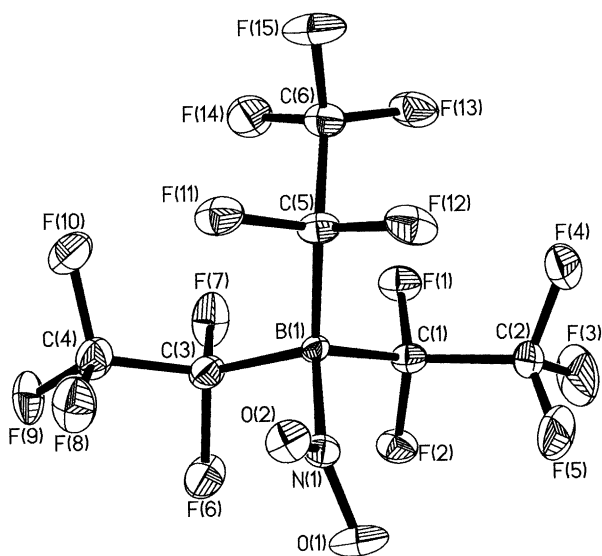


Fig. 1. A perspective drawing of an anion of **4a** using 20% probability thermal ellipsoids.

value for the identification of these species. The stretching frequencies decrease slightly with increasing bulkiness at boron. This might be associated with a weakening of the BN bond from [(CF₃)₃BNO₂]⁻ to [(C₂F₅)₃BNO₂]⁻, thus, placing more negative charge on the NO₂ group. However, the changes are small and the X-ray investigation is not sufficiently accurate to confirm such a weakening (*vide infra*).

2.2. Description of the crystal structure of **4a**

The two crystallographically independent anions in the asymmetric unit of **4a** exhibit no gross structural differences, and one of them is depicted in Fig. 1. While no disorder has been detected, the accuracy of the structure is limited by the large atomic displacements apparently exhibited by some of the fluorine atoms. In fact, the variation of chemically equivalent bond lengths is generally twice as large as would be expected from the standard deviations which were determined by least-squares techniques; therefore, in the following discussion we will cite standard deviations which have been derived from the spread of chemically equivalent parameters.

Selected inter-atomic distances and bond angles are presented in Table 3. The lengths of the average B–N

Table 3
Selected bond lengths (Å) and angles (°) for **4a**

B(1)–N(1)	1.613(9)	B(2)–N(2)	1.645(9)
B(1)–C(1)	1.623(10)	B(2)–C(7)	1.650(11)
B(1)–C(3)	1.651(10)	B(2)–C(9)	1.664(11)
B(1)–C(5)	1.675(10)	B(2)–C(11)	1.633(11)
C(1)–C(2)	1.550(12)	C(7)–C(8)	1.519(11)
C(3)–C(4)	1.483(12)	C(9)–C(10)	1.505(12)
C(5)–C(6)	1.510(10)	C(11)–C(12)	1.531(10)
N(1)–O(1)	1.218(7)	N(2)–O(3)	1.248(7)
N(1)–O(2)	1.230(8)	N(2)–O(4)	1.220(7)
N(1)–B(1)–C(1)	110.9(5)	N(2)–B(2)–C(7)	105.5(6)
N(1)–B(1)–C(3)	104.9(6)	N(2)–B(2)–C(9)	103.8(6)
N(1)–B(1)–C(5)	106.2(5)	N(2)–B(2)–C(11)	106.1(5)
C(1)–B(1)–C(3)	105.6(6)	C(7)–B(2)–C(9)	106.8(6)
C(1)–B(1)–C(5)	113.0(6)	C(7)–B(2)–C(11)	115.6(6)
C(3)–B(1)–C(5)	115.9(6)	C(9)–B(2)–C(11)	117.6(6)
B(1)–C(1)–C(2)	122.1(7)	B(2)–C(7)–C(8)	119.5(6)
B(1)–C(3)–C(4)	125.3(7)	B(2)–C(9)–C(10)	121.6(7)
B(1)–C(5)–C(6)	123.3(6)	B(2)–C(11)–C(12)	120.2(6)
O(1)–N(1)–O(2)	119.1(6)	O(3)–N(2)–O(4)	119.2(5)
O(1)–N(1)–B(1)	119.3(6)	O(3)–N(2)–B(2)	120.7(6)
O(2)–N(1)–B(1)	121.5(6)	O(4)–N(2)–B(2)	120.1(5)

[1.63(2) Å], B–C [1.65(2) Å] and N–O [1.229(14) Å] bonds in **4a** do not differ significantly from the corresponding values of 1.606(4), 1.618(10) and 1.223(13) Å reported for Cs[(CF₃)₃BNO₂] [3]. While in **4a**, the average C–C bond length of 1.52(2) Å appears normal, a large value of 122(2)° is found for the average B–C–C bond angle. Similarly large M–C–C angles have long been known in alkyl and (fluoroalkyl)metal complexes, and both electronic and steric interactions have been proposed in order to explain their occurrence [8].

In view of the *trans*-conformation of one N–B–C–C and two C–B–C–C chains of **4**, the geometry of the (C₂F₅)₃BN entity roughly conforms to C_s symmetry.¹ Each BNO₂ moiety is planar, and in both anions these planes are inclined by about 20° with respect to the symmetry planes of the (C₂F₅)₃BN fragments (e.g. the N(1)–B(1)–C(5) plane in Fig. 1). Contacts between the CF₃ groups occur on either side but not across the mirror plane, and evidence for the repulsive nature of these contacts is given by the systematics behind the large spread [12.0(8)°] of the C–B–C bond angles. Thus, the C(1)–B(1)–C(3) and C(7)–B(2)–C(9) angles, which are bisected by the mirror planes, have an average value [106.2(8)°] which is significantly smaller than that of the remaining C–B–C angles [average 116(2)°].

In this crystalline salt, the cations occupy cavities in the sublattice of the bulky anions. This results in fairly irregular cation coordination environments, and only those Cs–O and Cs–F interactions which are shorter than 4.0 Å are considered in the following discussion. The Cs(1) cation achieves

¹ Higher symmetries are conceivable for this fragment. If each N–B–C–C chain assumed a *trans*-conformation, C_{3v} symmetry (A) would be realized, or a quite different structure of C₃ symmetry (B) would be obtained if each CF₂ group would occupy a terminal position in only one antiperiplanar CF₂–B–CF₂–CF₃ chain.

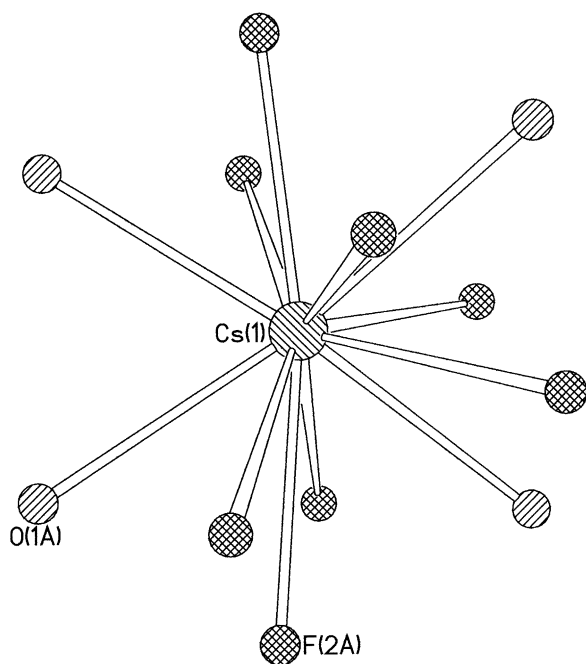


Fig. 2. A perspective drawing of the coordination sphere of the Cs(1) cation.

12 coordination by forming contacts with one oxygen and two fluorine atoms in each of four different anions (Fig. 2). An even less regular 13 coordination is found for the Cs(2) cation (Fig. 3). It forms four-membered chelate rings with two different nitro groups and makes contacts with three fluorine atoms in each of three other anions. These observations contrast with the cation coordination by the less bulky anion in Cs[(CF₃)₃BNO₂]. In that case, the Cs cation

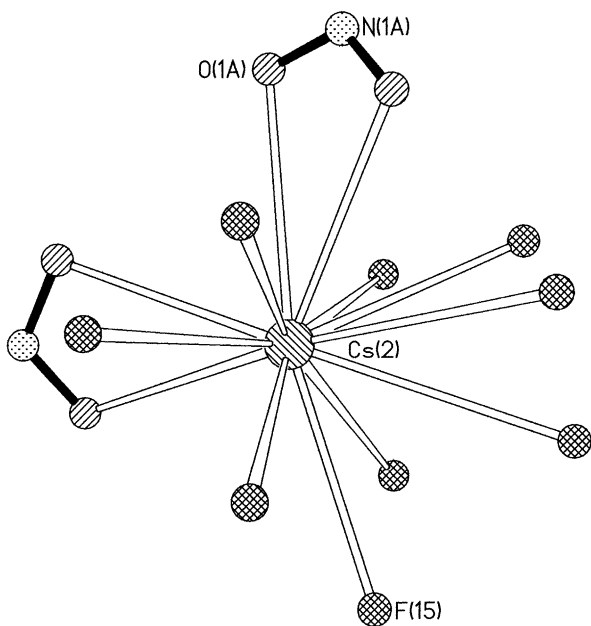


Fig. 3. A perspective drawing of the coordination sphere of the Cs(2) cation chelate nature of the nitro group.

Table 4
Interactions between anions and cations in Cs[R₃BNO₂] crystals

R	Bond	No.	Range (Å)	Σs_{ij}^b
C ₂ F ₅	Cs(1)–O	4	3.157(6)–3.265(5)	0.46
C ₂ F ₅	Cs(1)–F(CF ₂)	6	3.091(5)–3.246(5)	0.59
C ₂ F ₅	Cs(1)–F(CF ₃)	2	3.405(7)–3.421(6)	0.11
C ₂ F ₅	Cs(2)–O	4	3.236(5)–3.432(6)	0.35
C ₂ F ₅	Cs(2)–F(CF ₂)	5	3.356(6)–3.622(5)	0.25
C ₂ F ₅	Cs(2)–F(CF ₃)	4	3.342(6)–3.506(7)	0.23
CF ₃ ^a	Cs(1)–O	4	3.114(3)–3.534(3)	0.44
CF ₃ ^a	Cs(1)–F	10	3.166(3)–3.694(4)	0.42

^a [3].

^b Sum of bond valencies as calculated according to [9].

achieves 14 coordination by forming contacts with oxygen and fluorine atoms in seven different anions. Further details of these interactions are listed in Table 4.

While the Cs(2) cation exhibits a higher coordination number, these interactions tend to be longer than those formed by the Cs(1) ion. In order to better judge the importance of the contacts, a valence s was calculated for each contact distance r with the equation $s = \exp(r_0 - r)/B$. Here B is its standard value of 0.37, and r_0 values were taken from the compilations of Brown and Altermatt—being 2.417 and 2.328 Å for Cs–O and Cs–F contacts, respectively [9]. Valence sums are tallied for **4a** and Cs[(CF₃)₃BNO₂] in Table 4. A prominent trend in the calculated valencies is the importance of the Cs–O contacts which account for about 40% of the bond valence of each cation. The oxygen atoms are obviously the nucleophilic centers of the anions. Noteworthy also is the constancy of the contribution of the oxygen atoms to the cation bond valencies; the average of the sums are 0.21(2) for the six oxygen atoms in these two structures.

No fluorine atom in these structures contributes more than 0.15 to the cation bond valencies. While all the fluorine atoms in Cs[(CF₃)₃BNO₂] are found in the coordination sphere of the cation, only 15 of the 30 fluorine atoms in **4a** form contacts. Furthermore, although the fluorine atoms of the CF₃ groups are 50% more prevalent than those of the CF₂ groups and occupy the periphery of the anion, their total contribution to the bond valency of the cations only amounts to 40% of that made by the fluorine atoms of the CF₂ groups. Perhaps the inductive effect enhances the relative nucleophilicity of the fluorine atoms in α position to the boron atom. Because the sums of the bond valencies for Cs(1) (1.16) is markedly higher than that for Cs(2) (0.82), the latter should be bonded less tightly in the crystal. In line with this supposition, the equivalent isotropic thermal parameter of Cs(2) is 12% larger than that of Cs(1).

2.3. Resume

A simple analogy relates a neutral carbon atom with a boron atom bearing a negative charge. Transferred to perfluoroalkyl compounds, the nitroborates **2a–4a** have

their counterparts in the neutral species $(C_2F_5)_3CNO_2$, $C_2F_5(CF_3)_2CNO_2$, and $C_4F_9(CF_3)_2CNO_2$. To the best of our knowledge, these species are unknown, whereas derivatives $(C_2F_5)_3CX$ ($X = OH$ [10], F [11]), $C_2F_5(CF_3)_2CX$ ($X = H$ [12], OH [13], F [14,15], Br [16], I [17]), and $C_4F_9(CF_3)_2CX$ ($X = OH$ [18]) have been characterized. With increasing chain length of the perfluorinated unit R_f , the melting points of the Cs-nitroborates drop significantly compared with that of $Cs[(CF_3)_3BNO_2]$. This should also hold for other derivatives $Cs[R_f(CF_3)_2BX]$ where $X = F, OH, \dots$ and also for species where boron is connected to four perfluoroalkyl groups $Cs[R_f(CF_3)_3B]$. One can anticipate that especially the latter Cs-borates will be ionic waxes or liquids with outstanding thermal and chemical stability.

3. Experimental

3.1. General

NMR: Bruker ARX 400 (400, 100.6 and 376.5 MHz, for 1H , ^{13}C and ^{19}F , respectively), Bruker AC 250 (79.8 MHz for ^{11}B): $CDCl_3$ (1H : $\delta_H = 7.27$, ^{13}C : $\delta_C = 77.0$), $[D_3]$ -acetonitrile (1H : $\delta_H = 1.95$, ^{13}C : $\delta_C = 1.30$), $[D_6]$ acetone (1H : $\delta_H = 2.05$, ^{13}C : $\delta_C = 30.5$) as solvent and internal standard, ^{19}F : external standard $CFCl_3$, ^{11}B : external standard $BF_3 \cdot OEt_2$. IR: Bruker IFS 25; Raman: Bruker Equinox 55 (Laser 9394.8 cm^{-1}); MS: Varian MAT 311 (70 eV). Thermogravimetry: Netzsch STA 409. Ozone generator: Fischer 501.

3.2. X-ray structural determination

Crystals of **4a** were grown from aqueous solution, and one was glued to a glass fiber. X-ray data were measured with a P3 diffractometer employing $Mo\ K\alpha$ radiation and a graphite monochromator. Intensities were extracted from the profiles of the $\theta/2\theta$ scans and were corrected for the small drift of the three monitor reflections and absorption. Analysis of the Patterson function led to the coordinates of the cations, and a series of difference Fourier syntheses furnished the locations of the remaining atoms. The structure was refined to convergence by least-squares techniques using all data. The final value for the Flack parameter x , $-0.02(2)$, indicates that the absolute structure has been determined correctly [19]. Crystal data are given in Table 5. The structure was solved, refined and displayed using the Siemens SHELXTL, version 5.03, suite of programs. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC-173152. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.²

Table 5
Crystallographic data for **4a**

Empirical formula	$C_6BCSF_{15}NO_2$
Formula weight	546.79
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	12.776(2)
b (Å)	12.814(2)
c (Å)	17.377(2)
v (Å ³)	2844.8(7)
Z	8
D_{calc} (g cm ⁻³)	2.553
Radiation	$Mo\ K\alpha$
Wavelength (Å)	0.71073
T (K)	294(2)
Diffractometer	Siemens P3
Scan mode	Profile data from $\theta/2\theta$ scans
θ range (°)	2.25–25.05
Limiting indices	$0 \leq h \leq 15, 0 \leq k \leq 15, -20 \leq l \leq 20$
Reflections collected	5685
Unique	5034
R (int)	0.0189
Observed ($I > 2\sigma$)	4158
Crystal size (mm)	$0.42 \times 0.25 \times 0.14$
μ (mm ⁻¹)	2.788
Transmission	0.70166–0.52426
R_1 (all data)	0.0451
$w R_2$ (all data)	0.0826
Goodness-of-fit on F^2	1.010
Parameters	469
ΔF map (eÅ ⁻³)	0.76 to -0.46
Flack parameter	$-0.02(2)$

3.3. Preparation of compounds

3.3.1. Dimethylamine bis(trifluoromethyl) pentafluoroethylborane (**2**) and dimethylamine bis(trifluoromethyl)nonafluoro-*n*-butylborane (**3**)

To a stirred mixture of 17.7 g (91.7 mmol) of $(CF_3)_2BNMe_2$ (**1**), 63.6 g (258 mmol) of C_2F_5I (ABCR), and 200 ml of CH_2Cl_2 (distilled from P_4O_{10}) 36 g (179 mmol) of TDAE (Aldrich) were dropwise added at $-5\text{ }^\circ\text{C}$ and stirred for 20 min keeping the temperature at $0\text{ }^\circ\text{C}$. After warming to $20\text{ }^\circ\text{C}$, the reaction mixture was washed twice with 400 ml of 37% HCl, 100 ml of water, and 400 ml of saturated $Na_2S_2O_3$. The organic layer was distilled at $70\text{ }^\circ\text{C}$, 10^{-2} Torr to yield 18.4 g of a light yellow oil. The material was treated with a flow of ozone/oxygen for a few minutes and redistilled to yield 17.2 g (54.9 mmol) 60% of pure **2**.

Compound **3** was obtained analogously from 9.16 g (47.5 mmol) of **1**, 10 ml (57.8 mmol) of *n*- C_4F_9I (ABCR), and 11 g (55 mmol) of TDAE in 130 ml of CH_2Cl_2 . Slow distillation of the organic layer furnished two fractions; first 2.7 g of an oil which contained besides unidentified products ca. 70% of **3**, and second 12.3 g of a solid mp $36\text{ }^\circ\text{C}$ pure **3** (29.8 mmol) 63%. Compound **2**: $C_6H_7BF_{11}N$ calc.: H 2.25, C 23.03, N 4.48 found: H 2.31, C 23.09, N 4.39. The m/z (rel. int.): 294 $[M - F]^+$ (3), 144 $[F_3CBFNHMe_2]^+$ (4), 94 $[F_2BNHMe_2]^+$ (100), 44 $[C_2H_6N]^+$ (65). Raman (cm^{-1}): 3270 w (NH), 1480 m (CF), 734 s δ_s (C– CF_3), 710 s δ_s

² Fax: +44-1223-336-033 or E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk

(B–CF₃). Compound **3**: C₈H₇F₁₅N calc.: H 1.71, C 23.27, N 3.39 found: H 1.68, C 22.38, N 3.36. The *m/z* (rel. int.): 394 [M – F]⁺ (2), 294 [M – C₂F₅]⁺ (2), 244 [M – C₃F₇]⁺ (1), 94 [F₂BNHMe₂]⁺ (100). Raman (cm⁻¹): 3269 w (NH), 1484, 1460 m (CF), 772 δ_s (C–CF₃), 719 vs δ_s (B–CF₃).

3.3.2. Dimethylamine tris(pentafluoroethyl)borane (**4**)

To a stirred mixture of 6.55 g (30.5 mmol) of Br₂BNMe₂, 29.5 g (120 mmol) of C₂F₅I (ABCR) and 150 ml of CH₂Cl₂ (distilled from P₄O₁₀) 22 g (110 mmol) of TDAE (Aldrich) were dropwise added at –10 °C. The reaction mixture was stirred for 20 min at –5 °C and then allowed to warm to room temperature. Upon addition of 300 ml of 37% HCl, the organic layer was separated, washed with 100 ml of 37% HCl and then with 50 ml of water. The organic layer was distilled at 70 °C, 10⁻² Torr to yield a yellow oil. The oil was diluted with 30 ml of CHCl₃ and treated with a flow of ozone/oxygen until the yellowish color had disappeared and again slowly distilled at 45 °C, 10⁻² Torr. Yield 1.52 g of **4** (3.7 mmol) 12%. Compound **4**: C₈H₇BF₁₅N calc.: H 1.71, C 23.27, N 3.39 found: H 1.66, C 23.20, N 3.41. The *m/z* (rel. int.): 175 [CF₃CFBFNHMe₂]⁺ (21), 131 [C₃F₅]⁺ (12), 119 [C₂F₅]⁺ (8), 94 [F₂BNHMe₂]⁺ (100), 80 [FCBF₂]⁺ (83), 44 [C₂H₆N]⁺ (99).

3.3.3. Cesium bis(trifluoromethyl)pentafluoroethylnitroborate (**2a**), cesium bis(trifluoromethyl)nonafluoro-*n*-butylnitroborate (**3a**), cesium tris(pentafluoroethyl)nitroborate (**4a**)

A flow of ozone/oxygen (ca. 2 g O₃/h) was introduced into a stirred suspension of 10 mmol of **2**, **3**, or **4** in 80 ml of 25% CsOH at 60 °C through a Teflon PFA tube. The reaction was stopped when a clear solution was obtained. The reaction mixture was cooled to 4 °C in an ice bath upon which the Cs salts **2a–4a** crystallized. Re-crystallization from water furnished shed analytically pure material in yields of 80–90%.

Similar results were obtained when the crude products **2–4** were reacted with ozone.

- **2a**: BCsC₄F₁₁NO₂ calc.: C 10.75, N 3.14 found: C 10.69, H 3.20;
- **3a**: BCsC₆F₁₅NO₂ calc.: C 13.18, N 2.56 found: C 13.23, N 2.61;
- **4a**: BCsC₆F₁₅NO₂ calc.: C 13.18, N 2.56 found: C 13.15, N 2.49.

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